polymer papers

Quantitative evaluation of sequence distribution and stereoregularity in ethyl acrylate–methyl methacrylate copolymers by ^{13}C n.m.r. spectroscopy*

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^{13}C n.m.r. spectra (75 MHz) of ethyl acrylate (A)–methyl methacrylate (M) copolymers prepared by free radical polymerization at 50°C, were analysed in terms of sequence distribution and stereoregularity of monomer units along the macromolecular chains. Ethyl acrylate and methyl methacrylate centred triad molar fractions were determined from the α-CH$_3$, quaternary carbon and carbonyl group, resonance signals. The experimental sequence concentrations were in fairly good agreement with the values calculated from the terminal copolymerization model and Bernoullian statistics, with the statistical parameters P_{ij} determined from the reactivity ratios and the feed composition and the coisotacticity parameters $\sigma_{MM}=0.24$, $\sigma_{AA}=0.31$, $\sigma_{MA}=\sigma_{AM}=\sigma^*=0.41$.

(Keywords: sequence distribution; stereoregularity; ethyl acrylate; methyl methacrylate; ^{13}C n.m.r.)

INTRODUCTION

Acrylic formulations based on alkyl acrylate copolymers are of practical interest in the preparation of coatings, membranes, adhesives and sealants, because of the wide range of glass transition temperatures covered by an appropriate selection of the copolymer system, as well as by their excellent chemical and optical properties. The distribution of monomer sequences along the macromolecular chains and the stereochemical configuration of monomeric units are factors of great significance to their physico-chemical properties and industrial applications[1–3].

In a previous communication[4] we studied the free radical copolymerization of ethyl acrylate (A), with methyl methacrylate (M), at several temperatures in different media, determining the reactivity ratios from the ^{1}H n.m.r. spectra of copolymer samples with different compositions. In order to get a more accurate insight into the copolymerization mechanism, the microstructure and the stereochemical configuration of monomer sequences in the copolymer chains, the present work deals with an exhaustive analysis of the sequence distribution and stereochemistry of ethyl acrylate–methyl methacrylate copolymers by ^{13}C n.m.r. spectroscopy.

EXPERIMENTAL

Synthesis of copolymers

Ethyl acrylate (A)–methyl methacrylate (M) copolymers were prepared as described previously[4], by free radical copolymerization in bulk at high vacuum, using AIBN as free radical initiator with a concentration of 0.3 mol%. The reaction temperature was 50°C and the reaction time was adjusted to obtain conversions lower than 10 wt%. In this sense, a reaction time of 60 min was considered appropriate for copolymers prepared with a methyl methacrylate mole fraction in the feed (F_M) higher than 0.40, and 45 min for copolymers prepared with $F_M <$ 0.40. Poly(methyl methacrylate) and poly(ethyl acrylate) samples were prepared using the same experimental conditions.

Homopolymer and copolymer samples were isolated by pouring the reaction mixture into a large excess of cool methanol. The precipitated samples were filtered, redissolved in chloroform and reprecipitated as before, filtered and dried to constant weight under vacuum at room temperature.

N.m.r. spectra measurements

^{13}C n.m.r. spectra were recorded at 40°C on 25% (w/v) chloroform-D solutions, (TMS as internal reference), with a Varian XLR-300 spectrometer operating at 75.5 MHz, using a flip angle of 80° (pulse width of 13 μs), a relaxation delay of 4 s and inversed gated decoupling in the acquisition; spectral width of 16 kHz and 16 K data points. These conditions ensure the complete relaxation of all the ^{13}C nuclei analysed. The relative peak intensities were measured from peak areas calculated by means of the electronic integrator or by triangulation and planimetry.

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* Dedicated to Professor G. Martín Guzmán on the occasion of his 65th birthday

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RESULTS AND DISCUSSION

The ^{13}C n.m.r. spectra of several copolymer samples prepared with different feed composition, and of the corresponding homopolymers, are shown in *Figure 1*. The assignment of the resonance peaks has been made on the basis of results of the off-resonance decoupling and by comparison with spectra of analogous chemical groups taken from the literature[5–8]. It is known that the ^{13}C n.m.r. resonance signals of the carbonyl carbon of poly(alkyl acrylate)s in general do not give information regarding the stereochemical configuration of monomer sequences, but the backbone methylene carbon splits into signals assigned to tactic dyad or tetrad distribution[6–10].

It may be expected that in the experimental conditions of the present work, the free radical propagation gives rise to the formation of macromolecular chains with a stereochemical distribution of tactic sequences according to Bernoullian statistics[11–15]. On this assumption we have tentatively estimated the isotacticity parameter σ_{AA} as defined by Bovey and Tiers[16], from the integrated intensities of the skeletal β–CH_2– resonances (signals between 35.10δ and 36.00δ of the spectrum a of *Figure 1*), giving a value $\sigma_{AA} = 0.31$, somewhat lower than the isotacticity parameter of the free radical polymerization of methyl acrylate ($\sigma = 0.5$) reported by Kobayashi *et al.*[17].

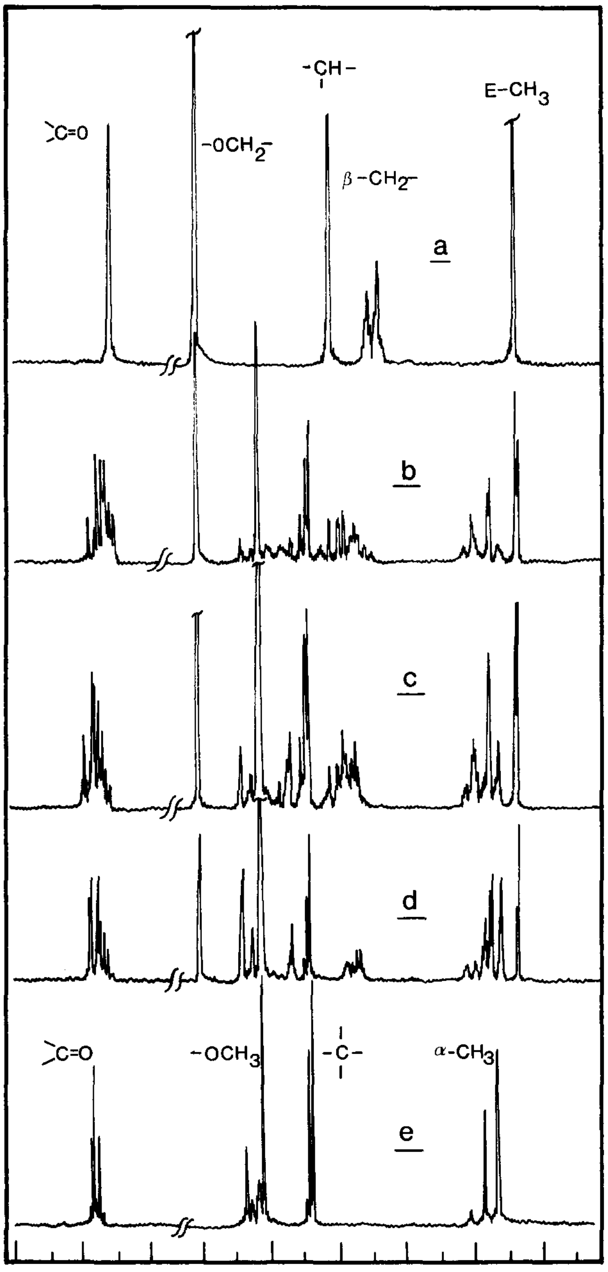

Figure 1 ^{13}C n.m.r. spectra (75 MHz) of homopolymer and copolymer samples prepared by free radical copolymerization of ethyl acrylate and methyl methacrylate at 50°C. Spectrum a, poly(ethyl acrylate); spectrum b, copolymer with $f_M = 0.48$; spectrum c, $f_M = 0.60$; spectrum d, $f_M = 0.80$; spectrum e, poly(methyl methacrylate)

Table 1 Experimental conversion, average composition and conditional probabilities P_{ij}, for the free radical copolymerization of ethyl acrylate with methyl methacrylate at 50°C. $P_{MM} = 1 - P_{MA}$ and $P_{AA} = 1 - P_{AM}$

F_M (feed)	f_M (copolymer)	Conversion wt%	P_{MA}	P_{AM}
0.800	0.89_7	7.90	0.10_6	0.96_6
0.700	0.85_2	7.46	0.16_9	0.94_3
0.600	0.80_3	8.19	0.24_0	0.91_5
0.500	0.72_8	9.03	0.32_2	0.87_7
0.400	0.68_9	8.41	0.41_6	0.82_7
0.300	0.60_0	8.70	0.52_4	0.75_4
0.200	0.48_0	9.26	0.65_5	0.64_1

Regarding the isotacticity parameter for the free radical polymerization of methyl methacrylate, from the analysis of the spectrum e of *Figure 1*, we obtain a value of $\sigma_{MM} = 0.24$, very close to that suggested by Kobayashi *et al.*[17] for the free radical copolymerization of methyl methacrylate with methyl acrylate ($\sigma_{MM} = 0.25$) which agrees with the value suggested by Bovey[18] for the free radical polymerization of methyl methacrylate in toluene at 50°C.

It can also be observed in the spectra in *Figure 1* that the $-OCH_2-$ and $-OCH_3$ resonances are not sensitive to the composition or the stereochemical configuration of copolymer samples, giving sharp peaks at 60.55δ and 51.13δ, respectively. Therefore, the average composition of copolymer samples prepared with ethyl acrylate molar fractions in the feed ranging from 0.2 to 0.8, were determined from the analysis of these resonance signals.

The results obtained are quoted in *Table 1*, together with the conversion percentage of copolymer samples. These in all cases are lower than 10 wt%, which permits us to apply the general copolymer equation, assuming that the copolymerization reaction follows the terminal unit model[19,20]. The application of the known Fineman–Ross[21] and Kelen–Tüdos[22] equations to these data gives the average values of the reactivity ratios: $r_M = 2.13 \pm 0.05$ and $r_A = 0.13 \pm 0.04$, in fairly good agreement with the values determined previously from the ^1H n.m.r. spectra of this copolymer system[4]. We also have calculated the conditional probabilities quoted in the fourth and fifth columns of *Table 1* (where P_{ij} $(i, j = M, A)$ are the conditional probabilities for the addition of monomer units j to free radical i ends)[23]. *Figure 2* presents the variation of the molar fraction of methyl methacrylate and ethyl acrylate centred triads as a function of methyl methacrylate molar fraction in the copolymer samples. The corresponding diagrams have been drawn on the basis of the terminal copolymerization model, with the values of P_{ij} quoted in *Table 1*. Note that the experimental points obtained from the analysis of the ^{13}C n.m.r.

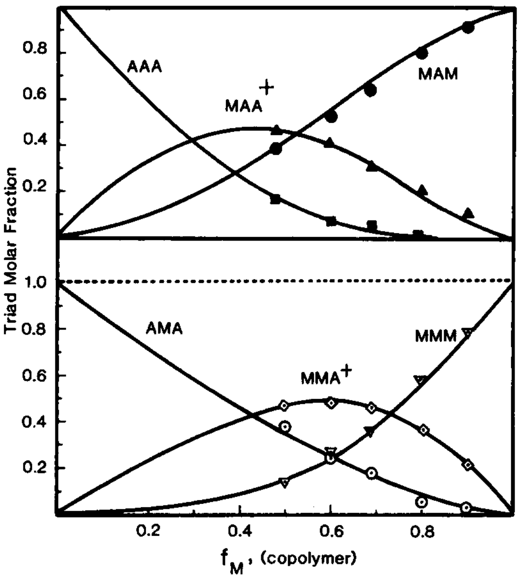

Figure 2 Distribution of ethyl acrylate (A) and methyl methacrylate (M) centred sequences, according to the terminal copolymerization model. The points correspond to experimental results obtained from n.m.r. spectra

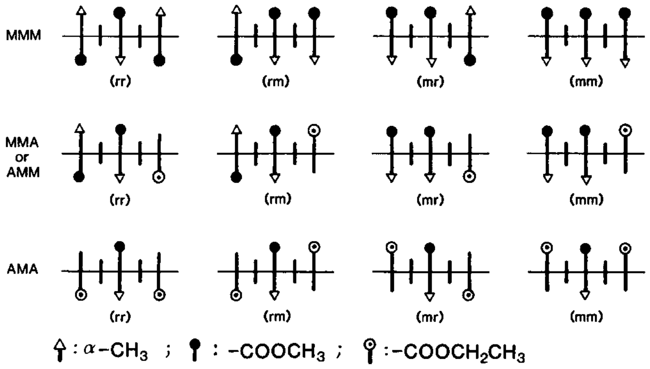

Figure 3 Schematic representation of M centred triads in ethyl acrylate–methyl methacrylate copolymers

spectra (by the sum of the contribution of the corresponding resonances, according to the assignment suggested later), fit adequately the diagrams calculated from the conditional probabilities, which makes clear that this system can be analysed on the basis of the classical copolymerization model.

For a complete description of the monomers sequence distribution and relative stereochemical configuration in terms of (M) and (A) centred triads, it is necessary to take into consideration as many as ten different triads with a central M unit which may be magnetically distinguishable, as is shown in the scheme of *Figure 3*. Similarly, ten triads with a central (A) unit must also be considered.

The statistical analysis of sequence distribution and stereochemical configuration of copolymer sequences has been carried out making the following assumptions.

With respect to the chemical composition of polymer sequences, it is considered that the copolymerization reaction is described by the terminal unit model[19,20].
From a stereochemical point of view we assume that the configurational sequence distribution may be described according to Bernoullian statistics with the isotacticity and coisotacticity parameters σ_{MM}, σ_{MA}, σ_{AM}, σ_{AA}, as defined by Bovey[16,18] and Coleman[24], where σ_{ij} is the probability of generating a meso dyad between an i ending growing radical and incoming j monomer. Values of $\sigma_{MM}=0.24$ and $\sigma_{AA}=0.31$, corresponding to the free radical polymerization of methyl methacrylate and ethyl acrylate, respectively, have been used. The coisotacticity parameters σ_{MA} and σ_{AM} are not accessible directly but it is reasonable to assume that $\sigma_{MA}=\sigma_{AM}=\sigma^*$ (refs 3, 25). This parameter can be determined from the analysis of the stereochemical configuration distribution derived from n.m.r. data.

In this sense we are interested in the resolution of the α–CH_3 and quaternary carbon of M centred sequences and the carbonyl group of both M and A centred sequences.

α–CH_3 resonance signals

The ^{13}C n.m.r. spectra drawn in *Figure 4* also show the resonance signals assigned to the α–CH_3 carbon of

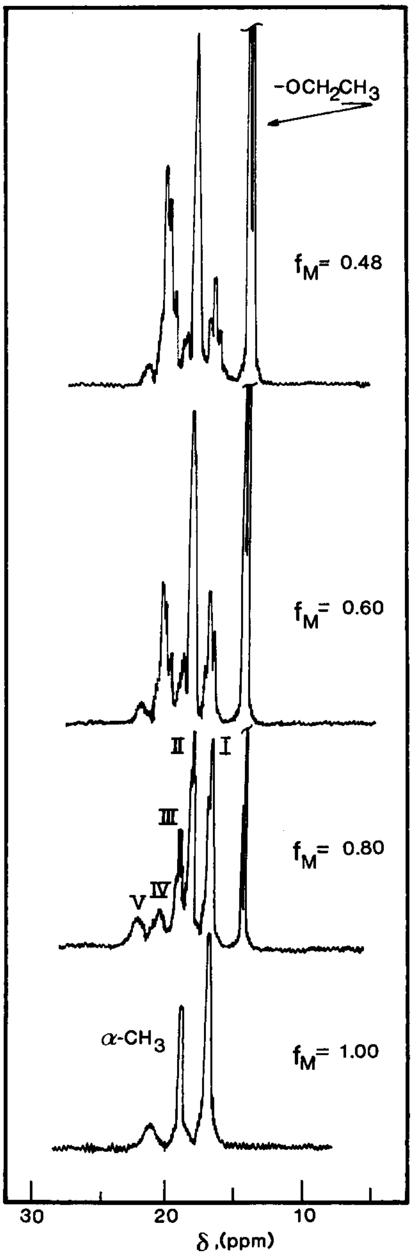

Figure 4 Expanded ^{13}C n.m.r. patterns of the α–CH_3 resonance signals of ethyl acrylate–methyl methacrylate copolymers

methyl methacrylate units. Analysis of the complex pattern between 15 and 22 ppm from TMS, permits us to define five resonance bands (named I to V in *Figure 4*), whose intensities change drastically with the composition of the copolymer samples. These signals have been analysed on the basis of methyl methacrylate centred triads, taking into account the stereochemical configuration (*Figure 2*).

From *Figure 4*, it can be easily seen that peaks I(16.40δ), III(18.80 δ) and V(21.50 δ) correspond to the chemical shifts of (rr), (mr or rm) and (mm) triads of poly(methyl methacrylate). Consequently, we have assigned these peaks to the same kind of MMM triads in the copolymer chains. The intensities of the two other signals II(17.80 δ) and IV(20.30 δ) increase with increasing ethyl acrylate mole fraction, allowing us to assign these signals to MMA or AMM and AMA triads, independently of the stereochemistry of triads. Note that all the resonance signals show further fine structure that cannot be analysed accurately, because of its complexity and poor resolution, but it is probable that they arise from the influence of the stereochemistry of MMA or AMM and AMA triads, or from the influence of longer sequences than triads. Nevertheless, it is possible to determine accurately the intensities of the resonance signals considered. *Figure 5* shows the variation of the mole fraction of methyl methacrylate centred triads as a function of the methyl methacrylate mole fraction. The experimental points correspond to the average values determined from the n.m.r. spectra, whereas the solid lines have been determined statistically using the statistical parameters P_{MA} and P_{AM} quoted in *Table 1*, as well as the isotacticity parameter σ_{MM}.

Quaternary carbon resonance signals

As can be clearly observed in the spectra b to e of *Figure 1*, the quaternary carbon of methyl methacrylate units gives rise to three well resolved peaks, whose intensities change with copolymer composition. Comparison with the resonance signals of this carbon atom in pure poly(methyl methacrylate), (spectrum e of *Figure 1*) suggests that they correspond to M centred triads independently of the composition but with the following stereochemical configuration: syndiotactic triads (rr), $\delta = 44.50$ ppm; heterotactic triads (mr or rm), $\delta = 45.00$ ppm; isotactic triads (mm), $\delta = 45.70$ ppm. From the integrated intensities of these signals we have determined a value of $\sigma^* = 0.41$ on the basis of Bernoullian statistics. This value is in the range of coisotacticity parameters reported for the free radical copolymerization of methyl methacrylate with other alkyl acrylic esters, because a value of $\sigma^* = 0.50$ has been reported by Kobayashi *et al.*[17] for the free radical copolymerization of methyl methacrylate with methyl acrylate, whereas Brosse *et al.*[26] suggest a $\sigma^* = 0.30$ for the free radical copolymerization of methyl methacrylate with butyl acrylate.

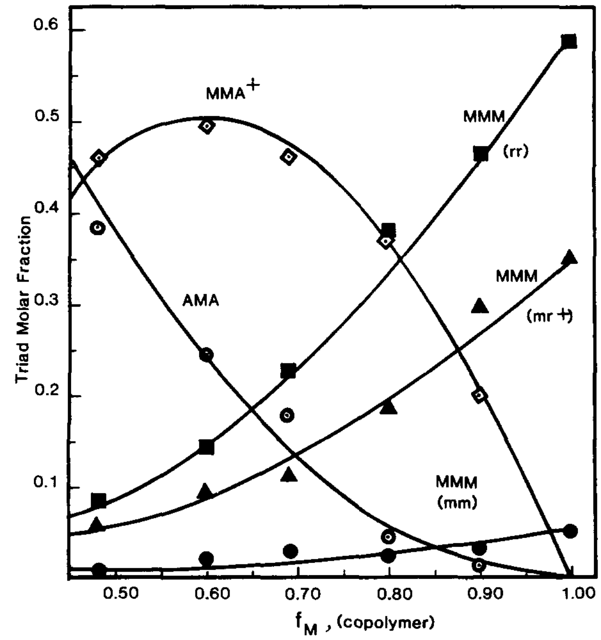

Figure 5 Variation of the concentration of M centred triads as a function of methyl methacrylate mole fraction in the copolymer samples

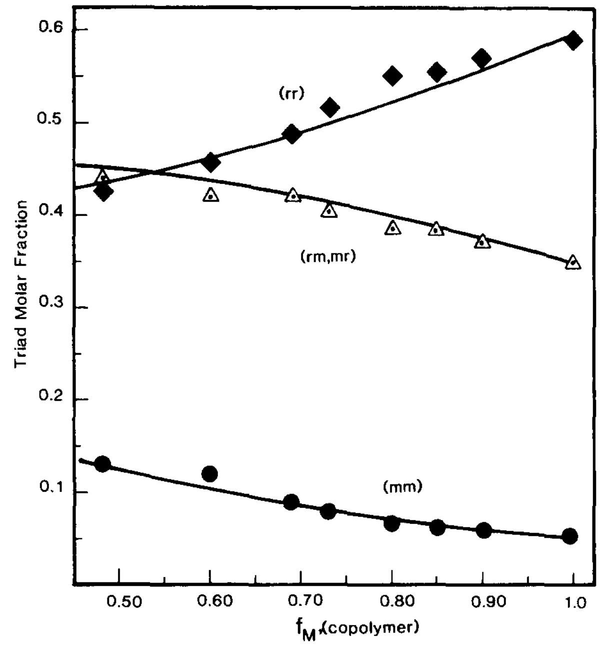

Figure 6 Variation of the concentration of stereochemical sequences (independently of the composition), vs. f_M

Figure 6 shows the variation of the molar fraction of methyl methacrylate centred triads (according to their stereochemical configuration but independently of the composition) as a function of the methyl methacrylate molar fraction in the copolymer samples. The points correspond to data obtained from the corresponding n.m.r. spectra; the lines have been drawn for Bernoullian statistics with isotacticity parameters $\sigma_{MM} = 0.24$ and $\sigma^* = 0.41$. The agreement between statistical diagrams and experimental points supports the assignment of n.m.r. signals and the validity of the stereochemical parameters established previously.

Carbonyl carbon resonance signals

We also have tested the validity of the statistical models considered, from the analysis of the complex pattern of carbonyl carbon resonance signals. *Figure 7* shows the spectra of the C=O resonances for three copolymer samples of different composition. As indicated, there are at least seven distinguishable signals (I to VII) and a little shoulder (named I′), whose intensities change drastically with the composition.

The assignment of these signals has been carried out

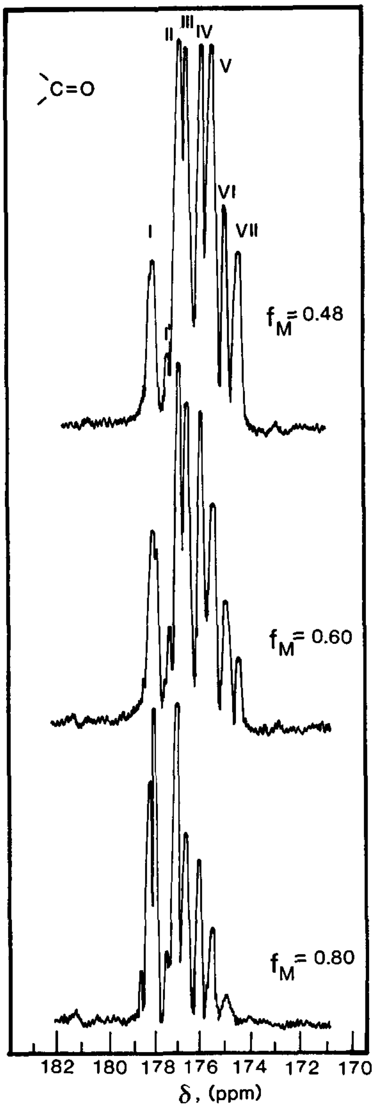

Figure 7 Expanded ^{13}C n.m.r. pattern of the carbonyl carbon resonance signals of M and A centred sequences

in terms of M and A centred triads, on the basis of the different chemical shift of the C=O group for poly(methyl methacrylate) (spectrum e of *Figure 1*) and poly(ethyl acrylate) (spectrum a of *Figure 1*). Accordingly, we considered that the ethyl acrylate centred triads are not sensitive to the configuration, whereas the methyl methacrylate centred triads may be sensitive to the stereochemical configuration of triad sequences. The comparison of the n.m.r. spectra of copolymers shown in *Figure 7* with those of the homopolymers (drawn in *Figure 1*) and the analysis of the variation of the corresponding relative intensities, permit us to suggest the assignment quoted in *Table 2*.

The peak at lowest field (peak I) is assigned to syndiotactic MMM homotriads (this peak is susceptible to analysis in terms of MMMMM stereochemical pentads for copolymers with f_M higher than 0.75). The substitution of one unit M by A in methyl methacrylate centred triads gives rise to a shift of the resonance signal about 1 ppm towards higher field. In view of molecular models and considering that the configuration meso or racemic of AM or MA pairs has little influence on the chemical shift of M centred triads (as it has been observed in the resonances of the α–CH_3), we suggest that the signals of triads MMA and AMM in which the pair MM presents a stereochemical configuration racemic, have chemical shifts close to MMM (mr or rm) triads. Therefore, we assign the peak II and the shoulder I' to the sequences indicated in *Table 2*. Similarly, the chemical shift of the resonances of MMA and AMM triads in which the pair MM presents a stereochemical configuration *meso*, would be very close to that of the MMM (mm) triads. Therefore we assign the peak IV to the triads indicated in *Table 2*. In this signal also is included the resonance of AMA (mm) and (mr + rm) triads, because it can be easily observed in the spectra that the difference of the chemical shift of peak IV with that of the MMM (rr) triads is very close to 2 ppm, which corresponds to the shielding effect of the two A units on the central M unit.

However, as we have observed in the resonances of the α–CH_3 groups, the steric interactions between the C=O groups of the A neighbours with the α–CH_3 group of the central M unit are very low so that, in AMA (rr) sequences, the magnetic character of the C=O groups may be very similar to that of the AAA sequences. Therefore we assign the peak VI to the mentioned AMA (rr) sequences.

With respect to the resonances of the carbonyl groups of A centred sequences, we assign the signal VII to AAA triads, independently of the stereochemical configuration of the sequences (because the chemical shift is coincident with that of poly(ethyl acrylate)) and the peaks III and V to MAM and MAA or AAM triads, respectively, as a consequence of the substitution of A units by M units in ethyl acrylate centred triads, independent of the stereochemical configuration. As for M centred triads, this substitution gives rise to resonance signals shifted about 1 ppm for each substitution, but in this case the M units cause a deshielding effect with respect to AAA triads.

On the basis of this assignment, in *Table 3* are quoted the values of the relative intensities of the resonance signals, together with the corresponding values calculated from the probabilities P_{ij} quoted in *Table 1* and the isotacticity parameters $\sigma_{MM} = 0.24$, $\sigma_{AA} = 0.31$ and $\sigma^* = 0.41$. The good agreement between the experimental and calculated values confirms the suggested assignment of the C=O resonances and the validity of the statistical parameters (P_{ij} and σ_{ij}) considered in the present work,

Table 2 Analysis and assignment of the resonance pattern of carbonyl carbon atoms of M and A centred sequences

Spectral signal number	Chemical shift (ppm)	Copolymer sequence	
		Composition	Configuration
I	177.85	MMM	(rr)
I'	177.30	MMM	(rm), (mr)
+		AMM	(mr), (rr)
II	177.00	MMA	(rm), (rr)
III	176.60	MAM	–
IV	176.00	MMM	(mm)
		MMA	(mr)
		AMM	(rm)
		AMA	(mm), (mr + rm)
V	175.50	AAM	–
		MAA	–
VI	175.00	AMA	(rr)
VII	174.60	AAA	–

Table 3 Experimental and calculated concentration of sequences, according to the assignment suggested in *Table 2*. The calculated values are the contribution of the corresponding molar fraction of triads according to the statistical and stereochemical parameters given in the text. The stereochemical pentads refer to pure M sequences

		f_M (copolymer)							
		0.897		0.803		0.600		0.480	
C=O peak no.	(ppm)	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
	178.40 (mrrm)	0.02_2	0.02_1	0.02_0	0.01_4				
I	178.10 (mrrr), (rrrm)	0.15_4	0.14_9	0.10_0	0.09_6	$0.10_6{}^a$	$0.08_3{}^a$	$0.04_3{}^a$	$0.03_7{}^a$
	177.85 (rrrr)	0.26_4	0.25_0	0.17_5	0.16_0				
I′ + II	177.30 177.00	0.39_0	0.39_0	0.36_0	0.38_9	0.26_3	0.28_8	0.20_7	0.19_1
III	176.60	0.11_0	0.09_0	0.16_7	0.17_0	0.20_1	0.22_0	0.19_1	0.20_0
IV	176.00	0.04_4	0.07_2	0.12_2	0.11_4	0.17_5	0.15_6	0.17_5	0.16_4
V	175.50	0.01_3	0.01_0	0.04_4	0.03_0	0.15_9	0.15_0	0.22_2	0.25_0
VI	175.00	0.00_3	0.00_4	0.01_2	0.01_7	0.06_8	0.05_6	0.09_1	0.07_0
VII	174.60	0.00_0	0.00_0	0.00_0	0.00_0	0.02_7	0.02_0	0.07_1	0.07_0

[a] These values correspond to the average contribution of the stereochemical pentads

according to the terminal model of copolymerization and Bernoullian stereochemical distribution of monomer units along the macromolecular chains.

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